



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 1d

Limestone, Argillaceous

This Standard Reference Material (SRM[®]) is intended primarily for use in evaluating chemical and instrumental methods of analysis of limestone and related materials. SRM 1d is composed of argillaceous limestone quarried in Putnam County, Indiana, USA. A unit of SRM 1d consists of a single bottle containing approximately 70 g of material of which 97 % passes a 75 μm (No. 200) sieve.

The certified values for 12 constituents in SRM 1d are listed in Table 1. Reference values for four constituents and loss on ignition (1000 °C) are listed in Table 2. Information values for 26 constituents and loss on ignition (1200 °C) are listed in Table 3. All values are reported as mass fractions [1] on a dry basis. Value assignment categories are based on the definition of terms and modes used at NIST for chemical reference materials [2], and uncertainties are assessed according to the ISO and NIST Guides [3]. Analytical methods employed in the development of this material are listed in Table 4.

Certified Values: A NIST certified value is a value for which NIST has the highest confidence in its accuracy, in that all known or suspected sources of bias have been investigated or accounted for by NIST. A certified value is the present best estimate of the true value based on the results of analyses performed at NIST and cooperating laboratories. The uncertainty listed with the value is an expanded uncertainty (95 % confidence interval [4]) and is calculated in conformance with the methods in the ISO and NIST Guides [3].

Reference Values: Reference values are non-certified values that are the present best estimates of the true values. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may not include all components of uncertainty. The uncertainty listed with the value is an expanded uncertainty (95 % confidence interval [4]) and is calculated in conformance with the methods in the ISO and NIST Guides [3].

Information Values: An information value is considered to be a value that will be of interest and use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value.

Constituent Assignment: The constituents listed in this Certificate of Analysis are expressed as the chemical forms given in ASTM C 25-99 [5]. Gravimetric factors used at NIST were calculated from the IUPAC recommended atomic weights [6].

Expiration of Certification: The certification of this SRM is valid until **01 October 2024**, within the uncertainty specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Use"). However, the certification will be nullified if the SRM is damaged or contaminated.

Stability: This material is considered to be stable during the period of certification when stored in its original container in a cool, dry location. NIST will monitor this material and will report any significant changes in certification to the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of the technical measurements leading to the certification of this SRM were performed by J.R. Sieber of the NIST Analytical Chemistry Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 18 February 2005

Robert L. Watters, Jr., Chief
Measurement Services Division

Analytical measurements for certification of this SRM were performed by J.R. Sieber and A.F. Marlow of the NIST Analytical Chemistry Division.

Statistical consultation was provided by S.D. Leigh of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

Material Preparation: The material for SRM 1d was obtained from Lone Star Industries, Inc.¹, Indianapolis, Indiana. The raw material was collected under the direction of W.D. Robinson, Lone Star Concrete, Greencastle, IN. Preparation of the SRM and contributing chemical analyses were performed by the U.S. Geological Survey (USGS) under the direction of S.A. Wilson. Homogeneity assessment was done by NIST using measurements performed at USGS.

INSTRUCTIONS FOR USE

To relate analytical determinations to the values on this Certificate of Analysis, a minimum sample quantity of 200 mg should be used. It is recommended to mix the contents of the bottle prior to sampling by turning the bottle end over end for two minutes. The sample should be dried according to the "Instructions for Drying". If particle size reduction is performed, it is the user's responsibility to prevent contamination or loss of material.

Instructions for Drying: The material must be dried at 105 °C to 110 °C in air for 2 h prior to analysis. Typical mass loss on drying is approximately 0.2 %.

Table 1. Certified Values for SRM 1d Limestone, Argillaceous

Constituent	Mass Fraction (%)	Expanded Uncertainty (%)
Na ₂ O	0.0109	0.0016 ^a
MgO	0.301	0.010 ^a
Al ₂ O ₃	0.526	0.013 ^a
SiO ₂	4.080	0.071 ^a
P ₂ O ₅	0.0413	0.0025 ^a
S	0.1028	0.0062 ^a
K ₂ O	0.1358	0.0046 ^a
CaO	52.85	0.16 ^a
Mn	0.0209	0.0005 ^a
Fe ₂ O ₃	0.3191	0.0068 ^a
ZnO	0.0022	0.0003 ^b
SrO	0.0303	0.0010 ^a

^a The assigned value is a weighted mean of the results from two to seven analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with a coverage factor 2 (approximately 95 % confidence), calculated by combining a between-source variance incorporating inter-method bias with a pooled within-source variance following the ISO and NIST Guides [3,7].

^b The assigned value is an unweighted mean of the results from two to five analytical methods. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance with a pooled, within-method variance following the ISO and NIST Guides [3,8].

¹ Certain commercial equipment, instruments, or materials are identified in this report to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 2. Reference Values for SRM 1d Limestone, Argillaceous

Constituent	Mass Fraction (%)	Expanded Uncertainty (%)
C	11.50	0.25 ^b
TiO ₂	0.0306	0.0065 ^b
Cr ₂ O ₃	0.0012	0.0002 ^b
BaO	0.0033	0.0011 ^b
Loss on Ignition (1000 °C)	41.57	0.06 ^a

^a The assigned value is a weighted mean of the results from two to seven analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with a coverage factor 2 (approximately 95 % confidence), calculated by combining a between-source variance incorporating inter-method bias with a pooled within-source variance following the ISO and NIST Guides [3,7].

^b The assigned value is an unweighted mean of the results from two to five analytical methods. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance with a pooled, within-method variance following the ISO and NIST Guides [3,8].

Table 3. Information Values for SRM 1d Limestone, Argillaceous

Constituent	Mass Fraction (mg/kg)	Constituent	Mass Fraction (mg/kg)
Be	0.1	Nb	0.7
Cd	0.3	Nd	3
Ce	4	Ni	4
Cl	130	Pr	0.6
Cs	0.4	Rb	6
Dy	0.6	Sm	0.5
Er	0.4	Sn	1
Eu	0.1	Tb	0.09
F	160	Th	0.5
Ga	1	U	1
Gd	0.5	V	10
Ho	0.1	Y	5
La	4	Yb	0.3
Loss on Ignition (1200 °C) ^c	41.6 %	Dry Brightness (Y) ^d	80.03

^c Note: Loss on Ignition [5] has units of %, not mg/kg.

^d Dry Brightness (Y) [9] is reported as a unit-less quantity.

Table 4. Analytical Methods Used in Elemental Determinations

Method	Constituents Determined
Wavelength Dispersive X-Ray Fluorescence Spectrometry (WDXRF) at NIST [10,11]	Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, Fe, Zn, Sr
Wavelength Dispersive X-Ray Fluorescence Spectrometry (WDXRF) at Cooperating Laboratories	Na, Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Zn, Sr, Ba
Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES) at Cooperating Laboratories	Be, Na, Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn, Sr, Sn, Ba
Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) at Cooperating Laboratories	Be, V, Ni, Ga, Rb, Y, Nb, Cd, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Th, U
Flame Atomic Absorption Spectrophotometry (FAAS) at Cooperating Laboratories	Na, K
Combustion with Infrared Detection at Cooperating Laboratories	C, S
Potentiometric Titration at Cooperating Laboratories	F, Cl

Cooperating Laboratories: Analytical determinations for certification of SRM 1d were performed by the following laboratories:

Acme Analytical, Laboratories Ltd.; Vancouver, British Columbia, Canada; R. McCaffrey, W. Szeto
Carmeuse Lime, Inc.; Annville, PA; J. Morrow
Carmeuse Technology Center; Pittsburgh, PA; M. Houghton
Construction Technology Laboratories, Inc.; Skokie, IL; D. Broton, M. Bharucha
Newmont Mining Corp.; Englewood, CO; C. Bucknam
Specialty Minerals, Inc.; Easton, PA; R. Kroc, G. Hevner, T. Rissmiller, G. Tomaino
United States Geological Survey; Denver, CO; S. Wilson, J. Taggart, Z. Brown, A. Meier, M. Adams, P. Briggs

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- [3] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed.; International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at <http://physics.nist.gov/Pubs/>.
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- [11] Sieber, J.R.; Broton, D.; Fales, C.; Leigh, S.; MacDonald, B.; Marlow, A.; Nettles, S.; Yen, J.; *Standard Reference Materials for Cements*; Cem. Concr. Res., Vol. 32, pp. 1899-1906 (2002).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; Fax (301) 926-4751; E-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>.